

JAPANESE

[JP,2002-075982,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD

PRIOR ART EFFECT OF THE INVENTION TECHNICAL

PROBLEM MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the coating composition which gives the semiconductor device containing the nature film of porous silica with a low dielectric constant, and the nature film of porous silica concerned, and the nature film of porous silica concerned.

[0002]

[Description of the Prior Art] A polysilazane film will be converted into a siliceous membrane if this is calcinated in the atmosphere. This siliceous membrane is excellent in electric insulation, and is used as an interlayer insulation film for semiconductors. Especially, since heat resistance is high and non-etchback is possible, the siliceous membrane of a perfect inorganic matter system is already used as an outstanding interlayer insulation film for semiconductors. In this case, the physical properties of a siliceous membrane are close to the thing of a silicon dioxide (SiO_2), and that specific inductive capacity is

in the range of 3.0-4.7.

[0003] An electronic industry material like the interlayer insulation film for semiconductors has too high [to respond to this request] specific inductive capacity by the conventional siliceous membrane, although much more lower dielectric constant-ization is demanded with improvement in the speed of an integrated circuit, and high integration. In order to reduce the specific inductive capacity of a siliceous membrane, porosity-izing a film is known, but generally a siliceous membrane has hygroscopicity and specific inductive capacity will rise with time under ambient environment. In order to prevent the rise of the specific inductive capacity by moisture absorption with the passage of time, it is possible to give a water-repellent finish which adds organic groups, such as a trimethylsilyl group, on the surface of a porous membrane, but it is not desirable to give such a water-repellent finish separately, in order to make a manufacturing cost increase.

[0004] How to porosity-ize the organic siliceous membrane obtained by calcination of a poly organicity silazane as an option which prevents the rise of such specific inductive capacity with the passage of time can be considered. By the structure which the organic group has linked with the silicon atom of silica directly, the water repellence of the film itself becomes high, and the rise of the specific inductive capacity by moisture absorption with the passage of time is suppressed, and the porous membrane possessing the heat resistance demanded as an interlayer insulation film for semiconductors and a resistance to environment is obtained.

[0005] Development of the groove-wires art for realizing more efficiently the minuteness making of internal wiring and the multilayering in a semiconductor device is also urged to the further high integration of the integrated circuit. With groove-wires art, a predetermined slot is beforehand formed in an interlayer insulation film so that it may be represented by damascene process, It is the art which forms groove wires by removing the wiring material which embedded wiring materials, such as an aluminum alloy and Cu, to the inside of a slot with the weld slag reflow method or the CVD method, and was further deposited outside the slot by the CMP (Chemical Mechanical Polishing) method etc. By progress of such groove-wires art, as for a semiconductor device, much more minuteness making of internal wiring becomes possible, and the further multilayering is attained by surface flattening by the CMP method.

[0006]

[Problem(s) to be Solved by the Invention] As opposed to the interlayer insulation film in which high integration of such an

integrated circuit exists between wiring, In addition to much more lower-dielectric-constant-izing, the mechanical strength which can bear the removal process of the wiring material by the CMP method is required, In the photoresist removal process by wet stripping besides the drugs furthermore used for the CMP method, the chemical resistance to various medicine, such as the drugs and drugs for removing the residue after ashing in the photoresist removal by ashing, is also required. However, since [for the problem of a rise of the specific inductive capacity by moisture absorption with the passage of time] the conventional porosity organicity silica membrane is not necessarily enough as above mechanical strengths or chemical resistance, these the demands of all cannot be filled with the conventional porous silica film.

[0007]Then, this invention shows stably very low specific inductive capacity (less than [Especially] 2.5), and it makes it a technical problem to provide the nature film of porous silica suitable for the interlayer insulation film which combines the mechanical strength which can bear the newest high integration processes including damascene process, and various chemical resistance. This invention also makes it a technical problem to provide the coating composition which gives such a nature film of porous silica.

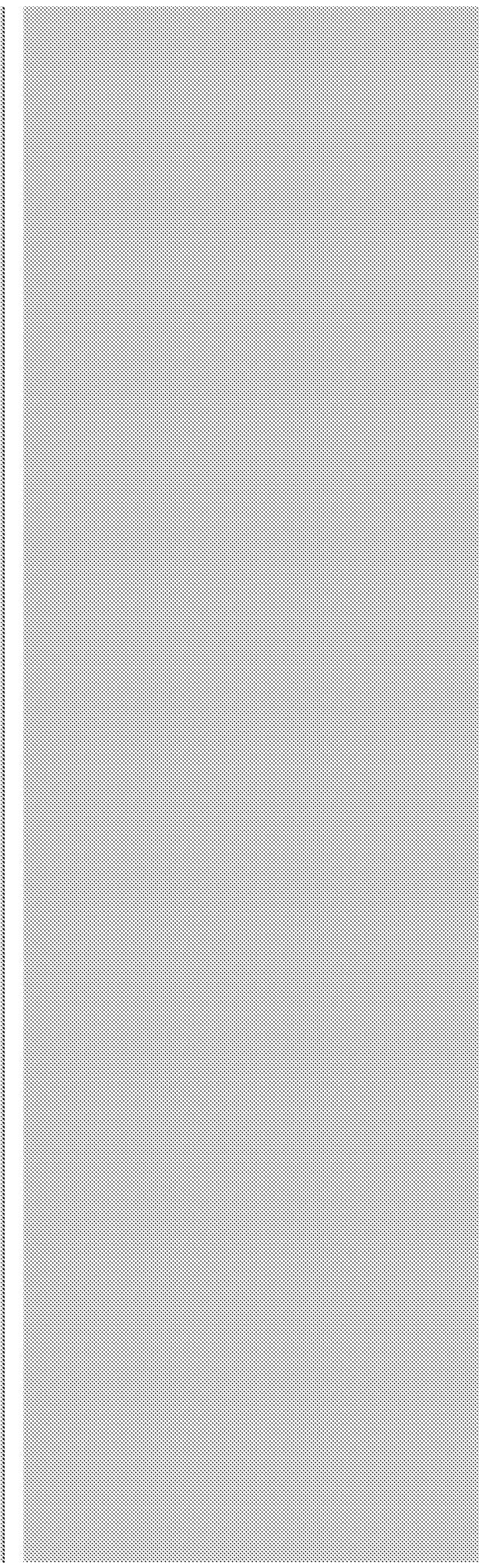
[0008]

[Means for Solving the Problem]This invention persons came to complete this invention, as a result of repeating research wholeheartedly that an aforementioned problem should be solved. That is, according to this invention, a nature film of porous silica, wherein specific inductive capacity obtained by calcinating a film of a constituent containing a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester is less than 2.5 is provided.

According to this invention, a semiconductor device by which said nature film of porous silica being included as an interlayer insulation film is provided. According to this invention, a coating composition which contains a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester in an organic solvent is provided. A poly alkyl silazane film which was produced by applying the coating composition concerned on a substrate according to this invention, Preliminary calcination is carried out in steam content atmosphere with a temperature of 50-300 **, and a manufacturing method of a nature film of porous silica calcinating in a drying atmosphere with a temperature of 300-500 ** subsequently is provided.

[0009]The desirable embodiment of this invention is as follows.

[1]A nature film of porous silica, wherein specific inductive capacity obtained by calcinating a film of a constituent containing a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid

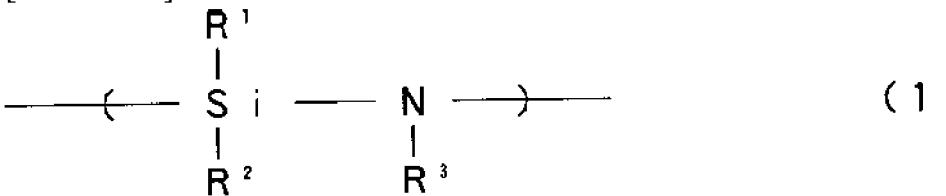


ester is less than 2.5.

[2]Said poly alkyl silazane is characterized by being a thing of the number average molecular weights 100-50,000 containing a repeating unit expressed with a following general formula (1) and/or a following general formula (2). [1]A nature film of porous silica given in a paragraph.

[0010]

[Formula 2]



[0011](R¹, R², and R³ express an alkyl group with a hydrogen atom or 1-3 carbon atoms independently respectively among an upper type.) However, the case where both R¹ and R² are hydrogen atoms is excluded.

- (SiR⁴(NR⁵)_{1.5}) - (2)

(R⁴ and R⁵ express an alkyl group with a hydrogen atom or 1-3 carbon atoms independently respectively among an upper type.) However, the case where both R⁴ and R⁵ are hydrogen atoms is excluded.

[3]In said general formula (1), it is characterized by R¹ and R² being a hydrogen atom or a methyl group, and R³'s being a hydrogen atom, and R⁴'s being a methyl group in said general formula (2) further, and R⁵ being a hydrogen atom. [2]The nature film of porous silica given in a paragraph.

[4]Said poly alkyl silazane both a repeating unit expressed with said general formula (1), and a repeating unit expressed with said general formula (2). It is characterized by being a thing of the number average molecular weights 100-50,000 included so that the number of repeating units expressed with said general formula (2) may have not less than 50% of a total of a repeating unit expressed with said general formula (1) and said general formula (2). [2]A nature film of porous silica given in a paragraph.

[5]The number of repeating units expressed with said general formula (2) has not less than 80% of a total of a repeating unit expressed with said general formula (1) and said general formula (2). [4]A nature film of porous silica given in a paragraph.

[6]It is characterized by said poly alkyl silazane being an aluminum content poly alkyl silazane. [1]A nature film of porous silica given in a paragraph.

[7]It is characterized by number average molecular weights of said polyacrylic ester or polymethacrylic acid ester being 1,000-

800,000. [1]A nature film of porous silica given in a paragraph. [0012][8]Quantity of said polyacrylic ester in said constituent or polymethacrylic acid ester is characterized by being 5 to 150 % of the weight to said poly alkyl silazane. [1]A nature film of porous silica given in a paragraph.

[9]Said constituent contains an aluminium compound further in 0.001 to 10% of the weight of the range to said poly alkyl silazane by the aluminum-metals equivalent unit concerned.[1]A nature film of porous silica given in a paragraph.

[10][1]-A semiconductor device by which a nature film of porous silica of a statement being included in any 1 paragraph of [9] as an interlayer insulation film.

[11]A coating composition which contains a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester in an organic solvent.

[12]A poly alkyl silazane film produced by applying on a substrate a coating composition which contains a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester in an organic solvent, A manufacturing method of a nature film of porous silica carrying out preliminary calcination in steam content atmosphere with a temperature of 50-300 **, and calcinating in a drying atmosphere with a temperature of 300-500 ** subsequently.

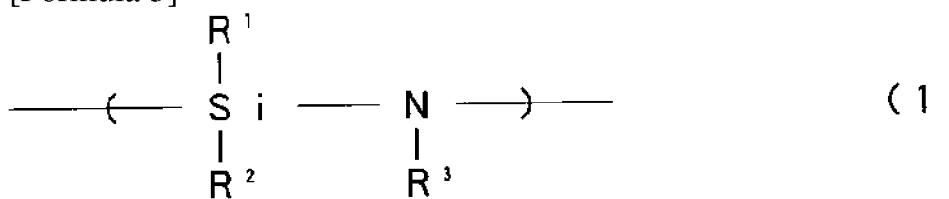
[13]It calcinates, after neglecting a poly alkyl silazane film after said preliminary calcination in atmospheric air. [12]A manufacturing method of a nature film of porous silica given in a paragraph.

[0013]

[Embodiment of the Invention]The nature film of porous silica by this invention is obtained by calcinating the film of the constituent containing a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester. As for the poly alkyl silazane concerned, it is preferred that it is a thing of the number average molecular weights 100-50,000 containing the repeating unit expressed with a following general formula (1) in the chain.

[0014]

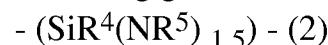
[Formula 3]



[0015] R^1 , R^2 , and R^3 express an alkyl group with a hydrogen atom or 1-3 carbon atoms independently respectively among an upper type. However, the case where both R^1 and R^2 are

hydrogen atoms is excluded. As an alkyl group, a methyl group, an ethyl group, and a propyl group are mentioned. Especially a suitable alkyl group is a methyl group. Since the porous membrane obtained becomes soft too much, the poly alkyl silazane which has four or more alkyl groups with a number of carbon atoms is not desirable. It is preferred for the poly alkyl silazane defined by the above-mentioned general formula (1) that R¹ and R² are a hydrogen atom or a methyl group (however, except for the case where both R¹ and R² are hydrogen atoms), and R³ is especially a hydrogen atom.

[0016]Especially it is based on this invention, a suitable poly alkyl silazane is a thing of the number average molecular weights 100-50,000 containing the repeating unit expressed with a following general formula (2) in the chain.



R⁴ and R⁵ express an alkyl group with a hydrogen atom or 1-3 carbon atoms independently respectively among an upper type. However, a case where both R⁴ and R⁵ are hydrogen atoms is excluded. About a definition of an alkyl group, it is the same as what explained a general formula (1) previously. R⁴ is a methyl group and especially a thing whose R⁵ is a hydrogen atom is preferred for a poly alkyl silazane defined by the above-mentioned general formula (2).

[0017]In this invention, a poly alkyl silazane containing a repeating unit of both the above-mentioned general formula (1) and (2) is useful at especially a point that gelling at the time of preservation of the constituent concerned can be prevented. In that case, it is preferred that the number of repeating units expressed with a general formula (2) is a thing of a total of a repeating unit expressed with a general formula (1) and a general formula (2) for which not less than 90% is occupied more preferably not less than 80% not less than 50%.

[0018]In an ammonolysis at the time of these poly alkyl silazanes compounding obvious usual polysilazane to a person skilled in the art, In the case of a poly alkyl silazane containing a repeating unit of a general formula (1), dialkyldichlorosilane (R¹R²SiCl₂), In the case of a poly alkyl silazane containing a repeating unit of a general formula (2), alkyl trichlorosilane (R⁴SiCl₃), And it is obtained by using a mixture of dialkyldichlorosilane and alkyl trichlorosilane as a starting material in the case of a poly alkyl silazane containing both repeating unit of these. In the case of a poly alkyl silazane containing a repeating unit of both a general formula (1) and (2), the mixture ratio of dialkyldichlorosilane and alkyl trichlorosilane determines an abundance ratio of both units.

[0019]If an aluminium compound of a gestalt which may dissolve in an organic solvent is added to an above-mentioned poly alkyl silazane, an aluminum content poly alkyl silazane which has not resulted in structure of an aluminio poly alkyl silazane which aluminum and silicon combined firmly will be obtained. An alkoxide, a chelation thing, organic aluminium, a halogenide, etc. are included by aluminium compound of a gestalt which may dissolve in an organic solvent. Although an addition of an aluminium compound is based also on the kind, it is an aluminum-metals equivalent unit and is 0.01 to 10 % of the weight preferably 0.001 to 10% of the weight to polysilazane. Refer to JP,11-105185,A for details about an aluminum content poly alkyl silazane.

[0020]A poly alkyl silazane by this invention is melted and used for an inert organic solvent which does not have active hydrogen preferably. As such an organic solvent, benzene, toluene, xylene, ethylbenzene, Aromatic hydrocarbon system solvents, such as diethylbenzene, trimethyl benzene, and triethylbenzene; Cyclohexane, A cyclohexene, deca PIDORO naphthalene, ethylcyclohexane, a methylcyclohexane, Ether system solvents, such as alicycle fellows hydrocarbon system solvent; dipropyl ether, such as p-MENCHIN and a dipentene (limonene), and dibutyl ether; ketone solvent, such as methyl isobutyl ketone, etc. are mentioned.

[0021]A coating composition by this invention is obtained by adding polyacrylic ester or polymethacrylic acid ester to an organic solvent solution containing a poly alkyl silazane mentioned above. In this invention, useful polyacrylic ester or polymethacrylic acid ester, Are a homopolymer or a copolymer of acrylic ester or methacrylic acid ester, and specifically, Polymethyl acrylate, polyethylacrylate, poly butyl acrylate, polymethylmethacrylate, polyethyl methacrylate, polybutyl methacrylate, poly isobutyl methacrylate, and these block copolymer and other copolymers are mentioned.

[0022]Polyacrylic ester or polymethacrylic acid ester by this invention uses that whose number average molecular weights are 1,000-800,000. A porous membrane is not formed in order that polyacrylic ester or polymethacrylic acid ester may sublime at low temperature that the molecular weight concerned is less than 1,000. If 800,000 is exceeded, an aperture will increase, and it becomes a cause of a void, a fall of film strength is caused, and neither is desirable. The ranges of a suitable molecular weight of polyacrylic ester by this invention or polymethacrylic acid ester are 10,000-600,000, and optimal result is obtained when it is especially 50,000-300,000.

[0023]An addition of polyacrylic ester by this invention or

polymethacrylic acid ester is made into 5 to 150 % of the weight to a poly alkyl silazane to be used. If there are few additions of polyacrylic ester or polymethacrylic acid ester than 5 % of the weight, membranous porosity-izing will become insufficient, if more on the contrary than 150 % of the weight, defects, such as a void and a crack, will occur on a film, film strength falls, and neither is desirable. The range of a suitable addition of polyacrylic ester by this invention or polymethacrylic acid ester is 10 to 120 % of the weight, and especially, when it is 20 to 100 % of the weight, optimal result is obtained.

[0024]When adding polyacrylic ester or polymethacrylic acid ester, generally the polyester concerned is added to a poly alkyl silazane solution with a gestalt of a solution melted into an organic solvent. In this case, what is necessary is just to use what was used for preparation of a poly alkyl silazane solution, and a common organic solvent as an organic solvent. That is, an inert organic solvent which does not have the above-mentioned active hydrogen as an organic solvent for dissolving polyacrylic ester or polymethacrylic acid ester is used. When melting and using polyacrylic ester or polymethacrylic acid ester for an organic solvent, concentration of polyacrylic ester or polymethacrylic acid ester can be preferably made into 10 to 40% of the weight of a range five to 80% of the weight. A homogeneous solution can be obtained by stirring physically after addition of polyacrylic ester or polymethacrylic acid ester. It is also possible to add and dissolve polyacrylic ester or polymethacrylic acid ester in a poly alkyl silazane solution as it is.

[0025]After an organic solvent solution containing a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester produced by making it above remains as it is or performs concentration regulation of a poly alkyl silazane, it can be used as a coating composition and can be applied to a base surface. As a coating method of a coating composition containing a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester to a base surface, a publicly known method, for example, a spin coat method, a dip method, a spray method, a replica method, etc. are mentioned conventionally.

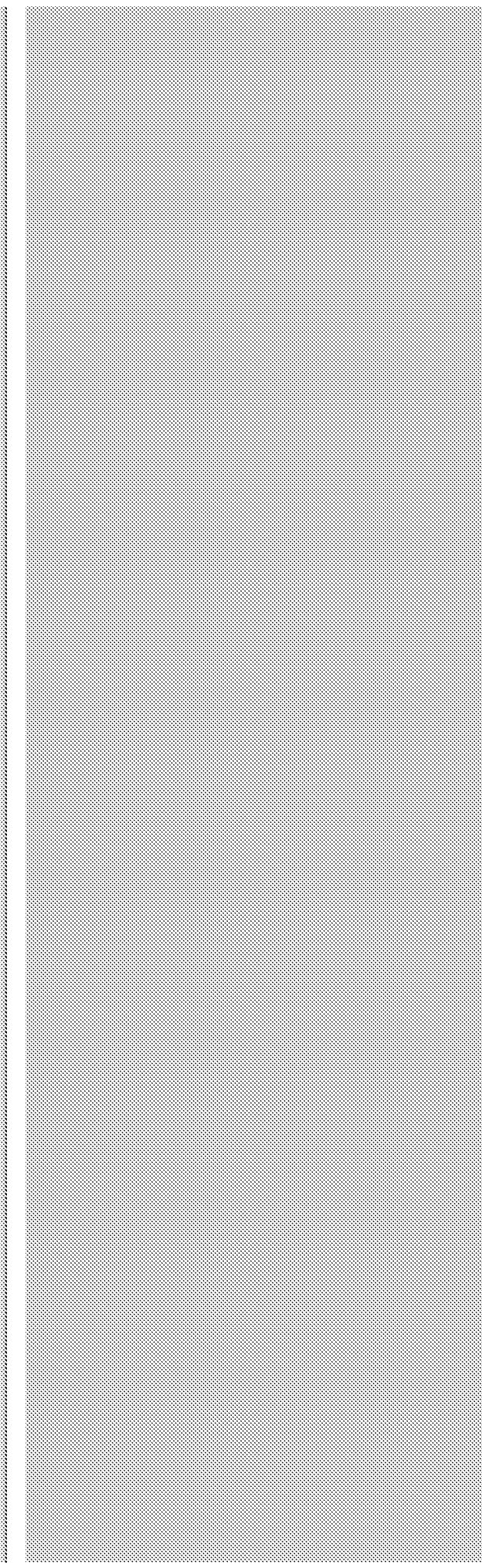
[0026]Calcination of a poly alkyl silazane film formed in a base surface is carried out in various kinds of atmosphere. Atmosphere which hardly contains steams, such as dry air, dry nitrogen, and dry helium, and atmosphere containing steams, such as the atmosphere, the humidification atmosphere, and humidification nitrogen, are included by atmosphere in this case. 50-600 ** of calcination temperature is 300-500 ** preferably, and firing time is 1 minute - 1 hour.

[0027]In order a dielectric constant is low and to manufacture a

good siliceous membrane of membranous quality advantageously by this invention. It is preferred to carry out preheating of this film in steam content atmosphere, to neglect it in atmospheric air subsequently for a long time (for example, 24 hours), after forming a poly alkyl silazane film in a base surface, and to carry out heating calcination in a drying atmosphere after that. In this case, as for steam content in steam content atmosphere, more than 0.1vol % is more than 1vol % preferably. The atmosphere, the humidification atmosphere, humidification nitrogen gas, etc. are mentioned to such an atmosphere. On the other hand, as for steam content in a drying atmosphere, below 0.5vol % is below 0.05vol % preferably. As a drying atmosphere, dry air, nitrogen gas, argon gas, gaseous helium, etc. are mentioned. Preheating temperature is 50-300 **. On the other hand, 100-500 ** of calcination temperature is 300-500 ** preferably.

[0028]According to the above-mentioned baking process, only SiN combination oxidizes among each combination of SiH in a poly alkyl silazane, SiR (R: hydrocarbon group), and SiN, it is converted into a SiO bond, and a siliceous membrane which has unoxidized SiH and SiR combination is formed. In particular, in heating calcination of an aluminum content poly alkyl silazane film, even if it does not perform prolonged neglect in atmospheric air, preferential oxidation reaction of SiN combination advances by a catalysis of aluminum. Thus, a SiO bond completed by SiN combination oxidizing selectively, and unoxidized SiH and SiR combination can be made to exist in a siliceous membrane formed, and, thereby, a siliceous membrane of low density can be obtained. Generally, although a dielectric constant of a siliceous membrane falls according to a fall of the film density, since adsorption of water which is quality of high dielectric things pledged will take place on the other hand if film density falls, if a siliceous membrane is neglected in the atmosphere, it will produce a problem that a membranous dielectric constant rises. On the other hand, in the case of a siliceous membrane of this invention including SiH and SiR combination, since those combination has water repellence, adsorption of water can be prevented though it is low density. Therefore, even if it neglects a siliceous membrane by this invention in the atmosphere containing a steam, a dielectric constant of the film has the big advantage of not carrying out a ***** rise. Since a siliceous membrane of this invention is low density, it also has an advantage that membranous internal stress is small and does not produce a crack easily.

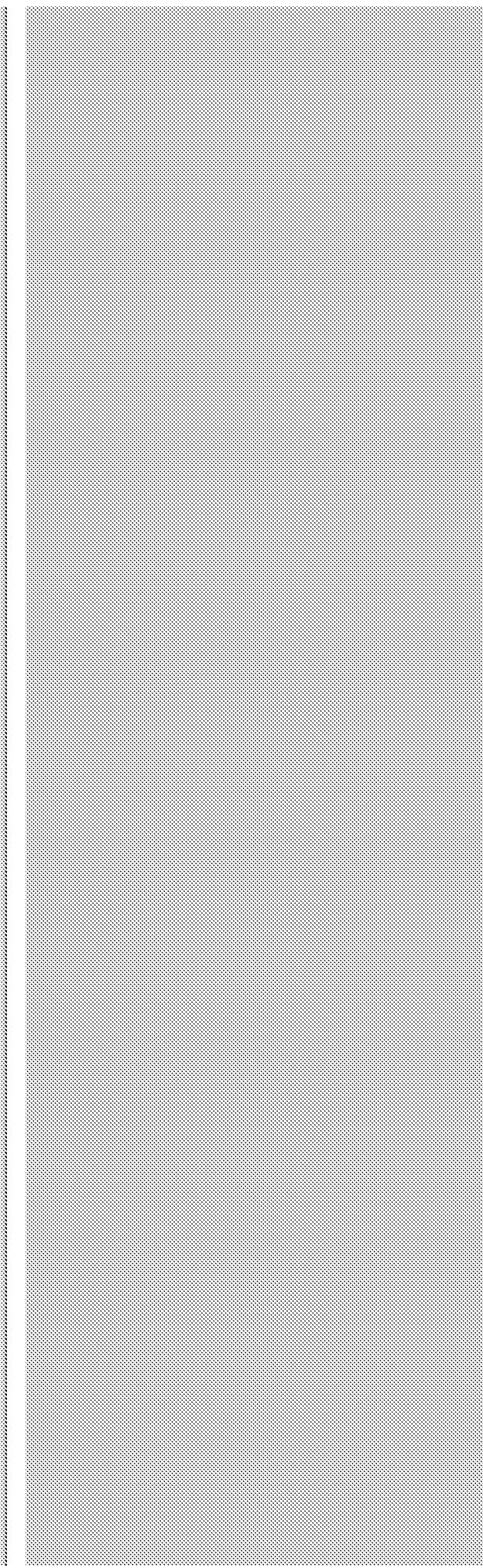
[0029]In calcination of said coating, when polyacrylic ester or polymethacrylic acid ester under coating sublimates, detailed fine



pores 5-30 nm in diameter are formed in an inside of a siliceous membrane. Density of a siliceous membrane will fall much more by existence of these fine pores, and, as a result, specific inductive capacity of a siliceous membrane will fall further. It is because this has very good compatibility with a poly alkyl silazane, polyacrylic ester, or polymethacrylic acid ester. Si-OH combination is prevented from generating in a poly alkyl silazane when calcinating the coating concerned by furthermore using polyacrylic ester or polymethacrylic acid ester. Therefore, a siliceous membrane by this invention holds above-mentioned water repellence, and even if it neglects it in the atmosphere containing a steam, specific inductive capacity which fell by fine pores hardly rises. Thus, low-density-izing and water-repellence-izing by a joint ingredient (SiH, SiR) of a siliceous membrane, [according to this invention] A nature film of porous silica in which low density-ization of the whole film by fine pores can hold stably conjointly very low specific inductive capacity called about 1.6 preferably less than 2.5 depending on 2.0 or less and the case is obtained. Therefore, an advantage as an inorganic material is not spoiled by introduction of an organic group except that a water-repellent finish which is generally needed for prevention from moisture absorption in the case of the conventional nature film of porous silica becomes unnecessary and becomes advantageous in respect of a manufacturing cost.

[0030] Since a nature film of porous silica by this invention has a mechanical strength and various chemical resistance which can bear a removal process of a wiring material by the CMP method, it can be used as an interlayer insulation film which suits the newest high integration processes including damascene process. A nature film of porous silica by this invention specifically, As a porous material of 2.5 or more GPa, a notably high mechanical strength is shown as an elastic modulus by the nano indentation method mentioned later, and. Various high chemical resistance called the following is hereafter shown by 0.8A/preferably by 1.0A/as an etching rate by etching residue release liquid etc. which are mentioned later.

[0031] When other descriptions of a nature film of porous silica by this invention are shown, the density 0.5 - 1.4 g/cm³, Preferably, 0.7-1.1g/[cm] ³ and its crack marginal thickness are not less than 10 micrometers, and 1.0 micrometers or more of the internal stress of below 2.0x10 ⁴N/cm² is below 1.0x10 ⁴N/cm². moreover -- as opposed to Si atomic number by which a Si content which exists as SiH contained in this siliceous membrane or SiR (R: hydrocarbon group) combination is contained in a film -- 10-100atom% -- it is 25-75atom% preferably. A Si content which exists as SiN combination is below pentatomic %. Although



thickness of a nature film of porous silica obtained after calcination changes also with uses of the base surface, it is usually 0.1-2 micrometers preferably 0.01-5 micrometers. When using as an interlayer insulation film of a semiconductor especially, it is 0.1-2 micrometers.

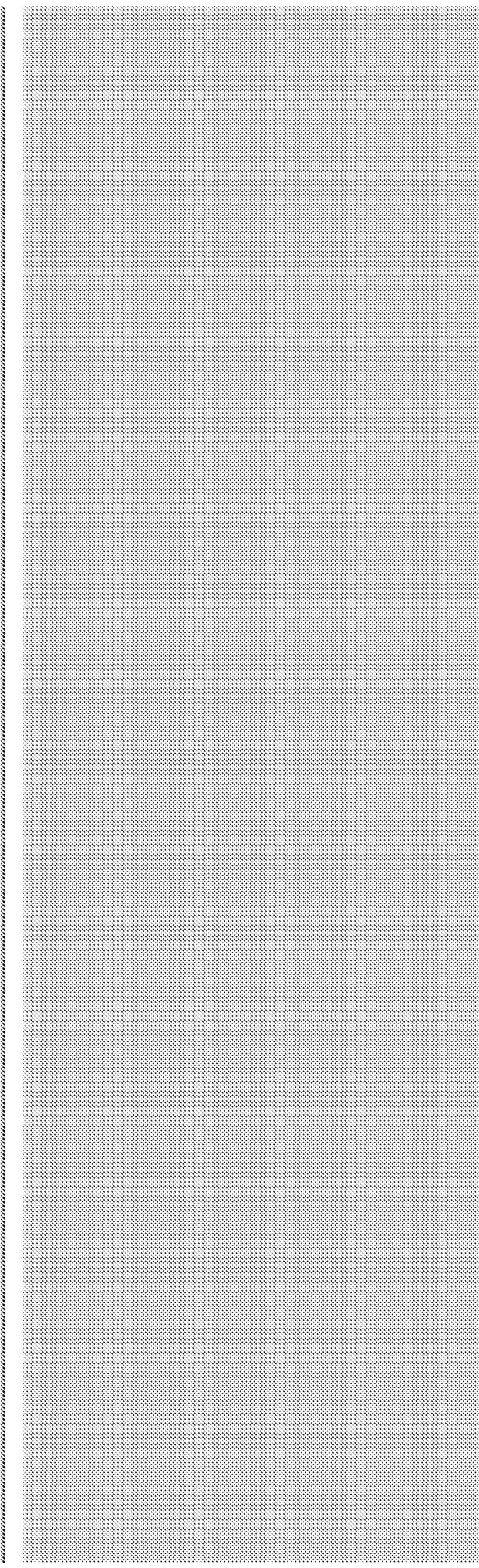
[0032]A nature film of porous silica by this invention is a thing of low density, as described above, and it also has the advantage that the maximum thickness which can produce a film is as high as not less than 5 micrometers without starting the crack marginal thickness, i.e., a film crack. In the case of the conventional siliceous membrane, the crack marginal thickness is about 0.5-1.5 micrometers. Therefore, a siliceous membrane of this invention shows a big technical effect compared with the conventional siliceous membrane.

[0033]This invention provides a nature film of porous silica which combines a stable lower dielectric constant, and a mechanical strength and various kinds of chemical resistance which can bear the newest fine wiring process with sufficient balance for the first time. By using a nature film of porous silica by this invention as an interlayer insulation film of a semiconductor device, the further high integration of an integrated circuit and multilayering are attained. Of course, a siliceous membrane can also be formed to a solid surface of various kinds of materials, such as metal, ceramics, wood, by using a coating composition of this invention besides an interlayer insulation film. a metal substrate (silicon.) which formed a siliceous membrane in the surface according to this invention SUS, tungsten, iron, copper, zinc, brass, aluminum, etc., Ceramics boards (metal nitrides, such as silicon nitride, boron nitride, titanium nitride, etc. besides metallic oxides, such as silica, alumina, magnesium oxide, titanium oxide, a zinc oxide, and tantalum oxide, silicon carbide, etc.) in which a siliceous membrane was formed on the surface are provided.

[0034]

[Example]Next, this invention is further explained in full detail according to an example. The valuation method of the physical properties shown about the siliceous membrane below is as follows.

[0035](Specific inductive capacity) The Dow Corning Pyrex glass board (1 mm in thickness, size of 50 mm x 50 mm) was often washed in order of neutral detergent, rare NaOH-aqueous-solution, and rare H₂SO₄ solution, and was dried. The Al film was formed with the vacuum deposition method all over this glass plate (0.2micro). After producing a poly alkyl silazane solution with a spin coat method to this glass plate, the four corners of the



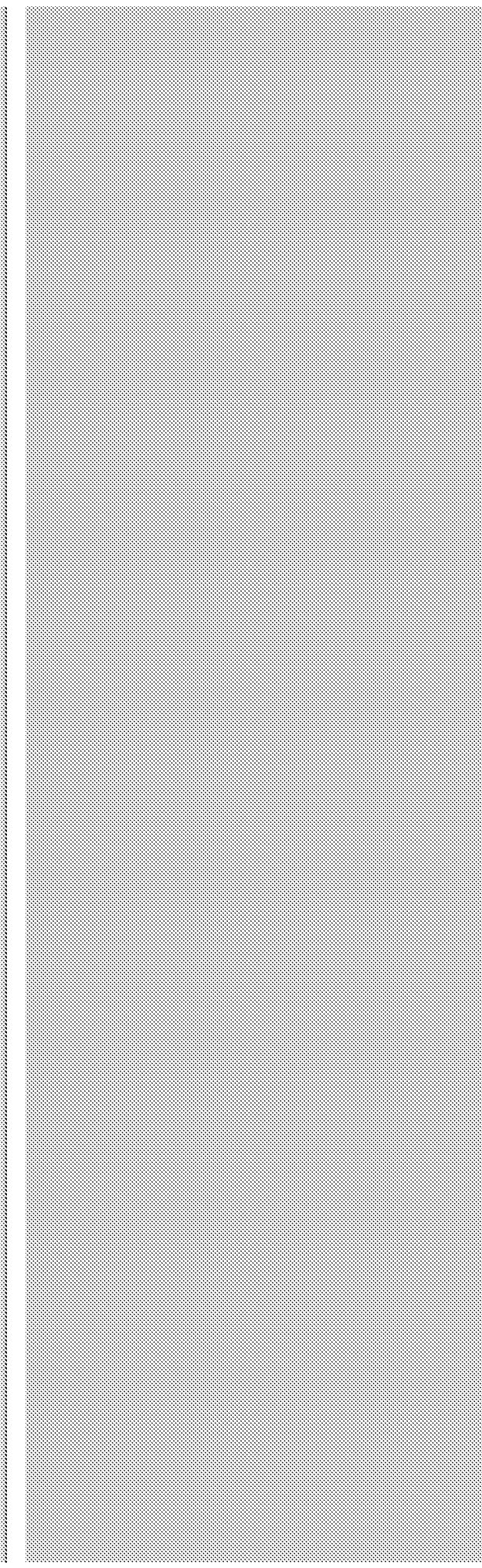
glass plate were rubbed with the cotton swab to electrode signal extraction, and the poly alkyl silazane film was removed. (About 3 mm x 3 mm). It continued and this was converted into the siliceous membrane in accordance with the method of an example or a comparative example. The mask made from SUS was put on the obtained siliceous membrane, and the Al film was formed with the vacuum deposition method (they are 18 pieces about a pattern (the square of 2 mm x 2 mm, and 2 micro in thickness)). Capacitance measurement was measured using the product made by YHP 4192ALF impedance analyzer (100 kHz). Thickness used the spectrum ellipsometer (J. the product made by A.Woollam, M-44). Specific inductive capacity was calculated by the lower type. Specific-inductive-capacity = (capacitance) [pF] x (thickness) [μm] /35.4, in addition the value of specific inductive capacity were made into the average value of 18 points.

[0036](Film density) The weight of the silicon wafer (4 inches in diameter and 0.5 mm in thickness) was measured with the electronic balance. After producing a poly alkyl silazane solution with a spin coat method to this, it converted into the siliceous membrane in accordance with the method of an example and a comparative example, and the weight of the silicon wafer with a film was again measured with the electronic balance. Film weight was made into these differences. Thickness was measured using the spectrum ellipsometer (J. the product made by A.Woollam, M-44) like specific-inductive-capacity evaluation. Film density was calculated by the lower type.

Film density [g/cm^3] (= Film weight) [g]/(thickness)

[μm])/0.008[0037](Internal stress) The camber of the silicon wafer (4 inches in diameter and 0.5 mm in thickness) was inputted into product [made by Tencor] laser internal-stress-measurement machine FLX-2320. After having converted into the siliceous membrane in accordance with the method of an example and a comparative example after producing a poly alkyl silazane solution with a spin coat method to this silicon wafer, and returning to a room temperature (23 **), internal stress was measured by product [made by Tencor] laser internal-stress-measurement machine FLX-2320. Thickness was measured using the spectrum ellipsometer (J. the product made by A.Woollam, M-44) like specific-inductive-capacity evaluation.

[0038](Crack marginal thickness) After producing a poly alkyl silazane solution with a spin coat method to a silicon wafer (4 inches in diameter, and 0.5 mm in thickness), it converted into the siliceous membrane in accordance with the method of an example and a comparative example. By adjusting the polysilazane concentration of a poly alkyl silazane solution, or the number of rotations of a spin coater, the sample to which thickness was



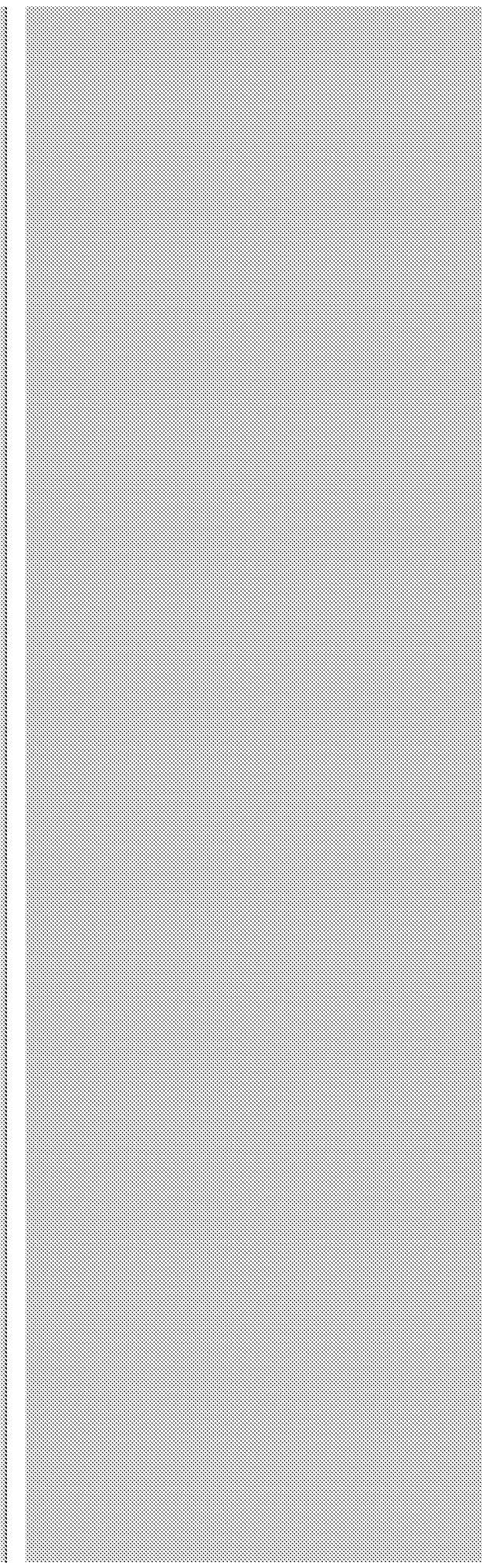
changed in about 0.5 to about 3 micro was produced. Microscope observation (x120) of the thin film after calcination was carried out, and the existence of the crack was investigated. The maximum thickness without a crack generation was made into crack marginal thickness.

[0039](An elastic modulus / the nano indentation method) After producing a poly alkyl silazane solution with a spin coat method to a silicon wafer (4 inches in diameter, and 0.5 mm in thickness), it converted into the siliceous membrane in accordance with the method of an example and a comparative example. About the obtained siliceous membrane, the elastic modulus by the mechanical property assessment system for thin films (the product made by NanoInstruments, Nano Indenter) was measured.

[0040](Etching rate) The etching rate measured thickness by the spectrum ellipsometer made from J.A.Woollam (M-44), and **(ed) and calculated it by drugs processing time (minute). The drugs used for etching rate measurement are shown in each below-mentioned example.

[0041]

Reference example 1[Composition (1) of a polymethylsilazane]
The tank reactor made from stainless steel of the content volume 5L was equipped with the stainless steel tank for feeding. After dry nitrogen replaced the inside of a reactor, 780 g of methyltrichlorosilane was put into the stainless steel tank for feeding, and this was fed and introduced into the reaction tank with nitrogen. Next, the feeding tank containing pyridine was connected to the reactor, and 4 kg of pyridine was similarly fed with nitrogen. The pressure of the reactor was adjusted to 1.0 kg/cm², and temperature control was performed so that the mixed solution temperature in a reactor might be -4 **. Ammonia was blown there, stirring, and ammonia supply was suspended when the pressure of the reactor became 2.0 kg/cm². The exhaust line was opened, reactor-vessel-pressure power was lowered, dry nitrogen was successingly blown into the solution layer for 1 hour, and excessive ammonia was removed. The acquired output was filtered under pressure under a dry nitrogen atmosphere using the pressure filter, and filtrate 3200mL was obtained. When pyridine was distilled off using the evaporator, about 340-g polymethylsilazane was obtained. When the number average molecular weight of the obtained polymethylsilazane was measured by GPC (developing solution: CHCl₃), it was 1800 in polystyrene conversion. IR (infrared absorption) spectrum showed the absorption based on Si-N-Si of absorption;1020 based on Si-C of absorption;2900 and 1250 based on N-H of the wave number (cm⁻¹) 3350 and the 1200 neighborhoods - 820.



[0042]

Reference example 2[Composition (2) of a polymethylsilazane]

As a raw material, instead of 780 g of methyltrichlorosilane, it compounded like the reference example 1 and about 370-g polymethylsilazane was obtained except for having used the mixture of 720 g of methyltrichlorosilane, and 65 g of dimethyldichlorosilane. When the number average molecular weight of the obtained polymethylsilazane was measured by GPC (developing solution: CHCl₃), it was 1400 in polystyrene

conversion. IR (infrared absorption) spectrum showed the absorption based on Si-N-Si of absorption; 1020 based on Si-C of absorption; 2900 and 1250 based on N-H of the wave number (cm⁻¹) 3350 and the 1200 neighborhoods - 820.

[0043]

Reference example 3[Composition of perhydropolysilazane]

The 4 mouth flask of the content volume 2L was equipped with the gas entrainment pipe, mechanical stirrer, and JUWA capacitor. After dry nitrogen replaced the inside of a reactor, 1500 ml of 4 mouth flask dry pyridine was put in, and this was ice-cooled. Next, when 100 g of dichlorosilane was added, the adduct (SiH₂Cl₂and2C₅H₅N) of the white solid state generated. The

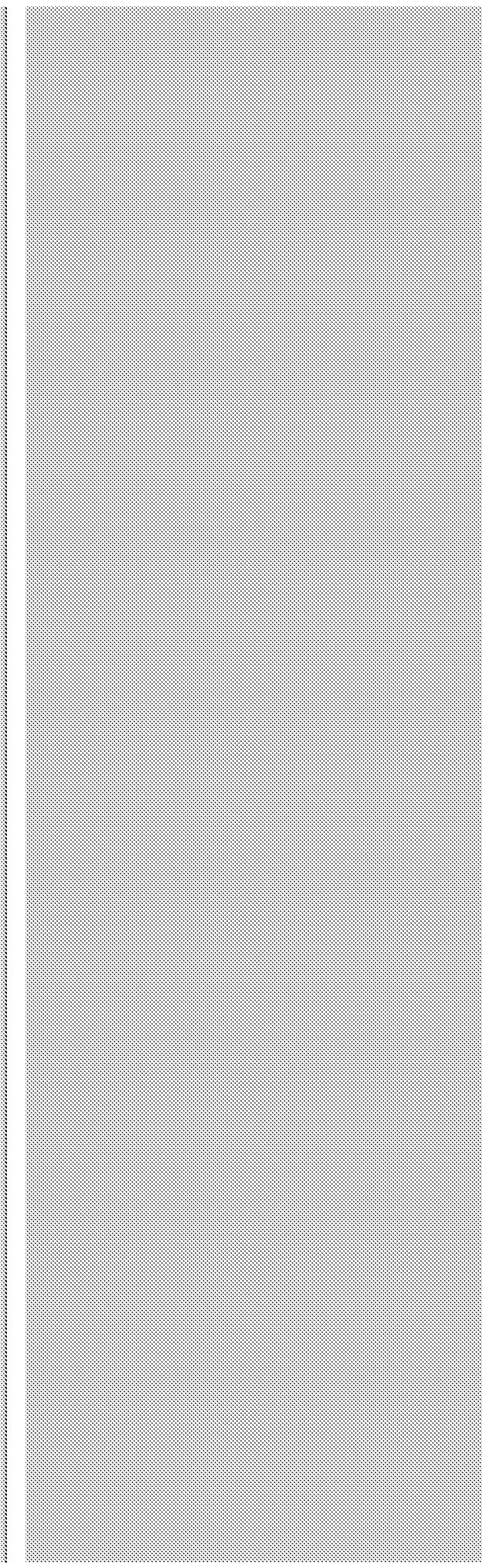
ammonia 70g was blown ice-cooling and stirring a reaction mixture. Dry nitrogen was successingly blown into the solution layer for 30 minutes, and excessive ammonia was removed. the acquired output -- BUFFUNA -- filtration under reduced pressure was carried out under a dry nitrogen atmosphere using the funnel, and 1200 ml of filtrate was obtained. When pyridine was distilled off using the evaporator, 40 g of perhydropolysilazane was obtained. When the number average molecular weight of the obtained perhydropolysilazane was measured by GPC (developing solution: CDCl₃), it was 800 in polystyrene

conversion. Absorption based on N-H of the wave number (cm⁻¹) 3350 and the 1200 neighborhoods in IR (infrared absorption) spectrum: The absorption based on Si-N-Si of absorption: 1020 based on Si-H of 2170 - 820 was shown.

[0044] In the 15% dibutyl ether solution 80g of the polymethylsilazane compounded by the example 1 (reference example 1 / poly isobutyl methacrylate =4:1) reference example 1. The above-mentioned polymethylsilazane solution was mixed and what dissolved well 3 g of poly isobutyl methacrylate of the molecular weight 160,000 [about] in the dibutyl ether 17g was stirred enough. Then, the solution was filtered with the PTFE syringe filter by ADVANTEC Co., Ltd. with a filtering accuracy of 0.2 micrometer. The spin coater was used and applied on the

silicon wafer (10.2 cm (4 inches) in diameter, and 0.5 mm in thickness) (2000 rpm, 20 seconds), and the filtrate was dried at the room temperature (5 minutes). Subsequently, the silicon wafer was heated for 3 minutes on a 280 ** hot plate to 150 ** and the next in atmospheric air (25 **, 40% of relative humidity), respectively. After neglecting this film in atmospheric air (25 **, 40% of relative humidity) for 24 hours, it calcinated for 30 minutes at 400 ** among a dry nitrogen atmosphere continuously. The absorption based on Si-O of the wave numbers (cm^{-1}) 1020 and 450 in IR (infrared absorption) spectrum, The absorption based on Si-C of the wave numbers (cm^{-1}) 1270 and 780, The absorption based on C-H of the wave number (cm^{-1}) 2970 was mainly seen, and the absorption based on N-H of the wave numbers (cm^{-1}) 3350 and 1200 and the absorption based on poly isobutyl methacrylate disappeared. When the obtained film was evaluated, as for 2.2 and density, $3.0 \times 10^8 \text{ dyne/cm}^2$ and the crack marginal thickness of 1.0 g/cm^3 and internal stress were [specific inductive capacity] not less than 5 micrometers. After neglecting the obtained film for one week in the atmosphere of the temperature of 23 **, and 50% of relative humidity, when specific inductive capacity was measured again, it was completely changeless. The elastic moduli by the nano indentation method of this film were 2.6GPa. ACT-970 widely used as etching residue release liquid (made by Ashland Chemical), The place which did the tolerance (compatibility) examination of the siliceous membrane using ST-210, ST-250 (made by ATMI), EKC265, and EKC640 (made by EKC), The etching rate was the following by 0.7A/, respectively, and the rise of the dielectric constant by the examination concerned was also less than 1.3%.

[0045]In the 20% dibutyl ether solution 160g of the polymethylsilazane compounded by the example 2 (reference example 2/BR1122=2:1, aluminum tris (ethylacetacetate)) reference example 2. The above-mentioned polymethylsilazane solution was mixed and what dissolved well 8 g of methacrylate (Mitsubishi Rayon BR1122) in the dibutyl ether 32g was stirred enough. Subsequently, mix 5 g of aluminum tris (ethylacetacetate) to the dibutyl ether 95g, it was made to dissolve, 24 g was taken out from the inside, the polymethylsilazane solution was mixed, and it stirred enough. Then, the solution was filtered with the PTFE syringe filter by ADVANTEC Co., Ltd. with a filtering accuracy of 0.2 micrometer. The spin coater was used and applied on the silicon wafer (20.3 cm (8 inches) in diameter, and 1 mm in thickness) (2000 rpm, 20 seconds), and the filtrate was dried at the room temperature (5 minutes). Subsequently, the silicon wafer was

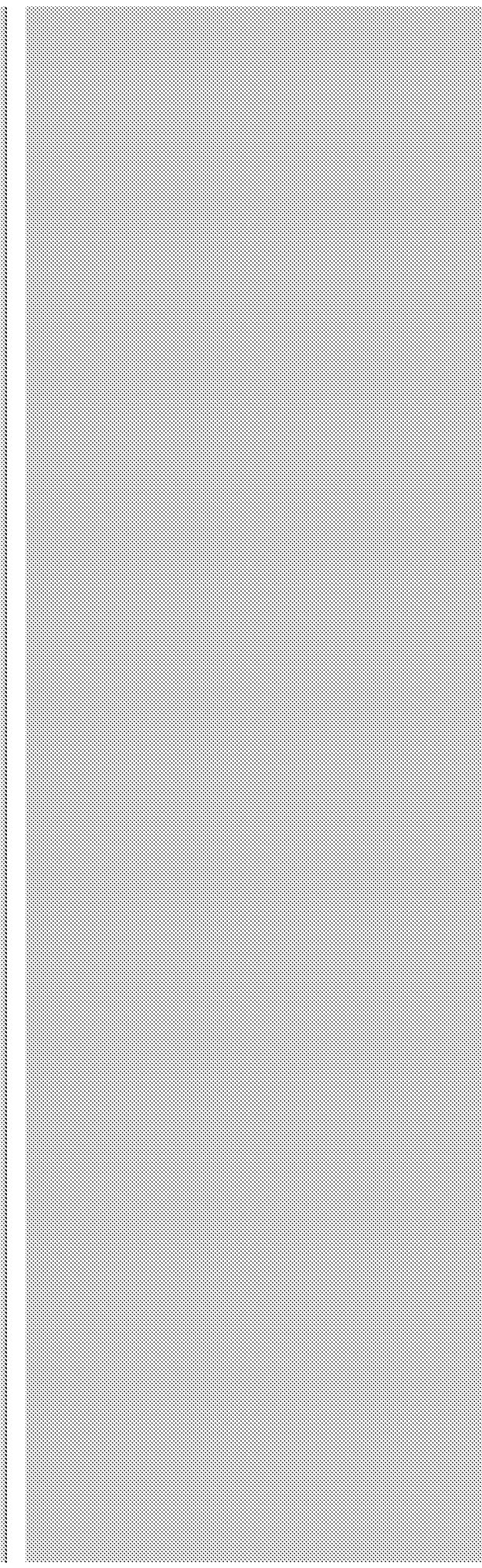


heated for 3 minutes on the hot plate (220 ** and 280 more **) to 150 ** and the next in atmospheric air (25 **, 40% of relative humidity), respectively. This film was calcinated for 10 minutes at 400 ** among a dry nitrogen atmosphere. The absorption based on Si-O of the wave numbers (cm^{-1}) 1020 and 450 in IR (infrared absorption) spectrum, The absorption based on Si-C of the wave numbers (cm^{-1}) 1280 and 780 and the absorption based on C-H of the wave number (cm^{-1}) 2980 were mainly seen, and the absorption based on N-H of the wave numbers (cm^{-1}) 3350 and 1200 and the absorption based on BR1122 disappeared. When the obtained film was evaluated, as for 2.1 and density, 2.8×10^8 dyne/ cm^2 and the crack marginal thickness of 0.9 g/cm^3 and internal stress were [specific inductive capacity] not less than 5 micrometers. After neglecting the obtained film for one week in the atmosphere of the temperature of 23 **, and 50% of relative humidity, when specific inductive capacity was measured again, it was completely changeless. The elastic moduli by the nano indentation method of this film were 2.5GPa. ACT-970 widely used as etching residue release liquid (made by Ashland Chemical), When the compatibility examination of the siliceous membrane was done using ST-210 and ST-250 (made by ATMI), the etching rate was the following by 0.8A/, respectively, and the rise of the dielectric constant by the examination concerned was also less than 1.6%.

[0046]

In the 16% dibutyl ether solution 90g of the polymethylsilazane compounded by the example 3 (reference example 1/ PnBMA=3:1) reference example 1. The above-mentioned polymethylsilazane solution was mixed and the 16% dibutyl ether solution 30g of the poly n-butyl methacrylate of the molecular weight 140,000 [about] was stirred enough. Then, the solution was filtered with the PTFE syringe filter by ADVANTEC Co., Ltd. with a filtering accuracy of 0.2 micrometer. The spin coater was used and applied on the silicon wafer (20.3 cm (8 inches) in diameter, and 1 mm in thickness) (2200 rpm, 20 seconds), and the filtrate was dried at the room temperature (5 minutes).

Subsequently, the silicon wafer was heated for 3 minutes on a 280 ** hot plate to 150 ** and the next in atmospheric air (25 **, 40% of relative humidity), respectively. After neglecting this film in atmospheric air (22.5 **, 54% of relative humidity) for 24 hours, it calcinated for 10 minutes at 400 ** among a dry nitrogen atmosphere continuously. The absorption based on Si-O of the wave numbers (cm^{-1}) 1020 and 450 in IR (infrared absorption) spectrum, The absorption based on Si-C of the wave numbers (cm^{-1}) 1270 and 780, The absorption based on C-H of the wave



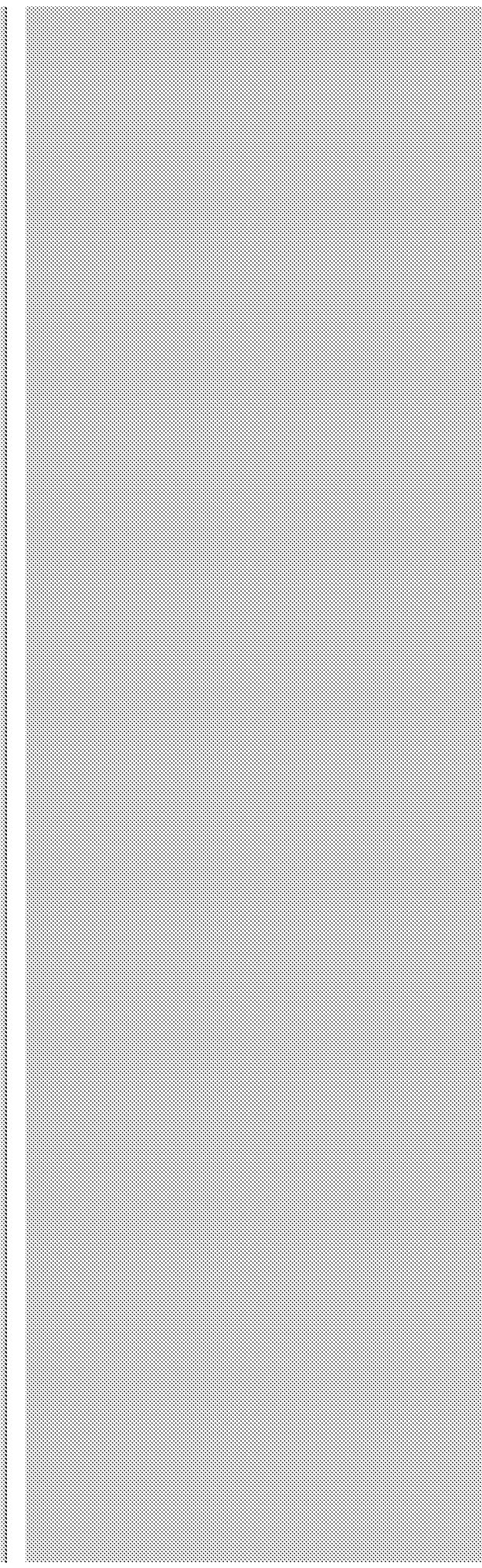
number (cm^{-1}) 2970 was mainly seen, and the absorption based on N-H of the wave numbers (cm^{-1}) 3350 and 1200 and the absorption based on poly n-butyl methacrylate disappeared. When the obtained film was evaluated, as for 2.0 and density, $2.8 \times 10^8 \text{ dyne/cm}^2$ and the crack marginal thickness of 1.0 g/cm^3 and internal stress were [specific inductive capacity] not less than 5 micrometers. After neglecting the obtained film for one week in the atmosphere of the temperature of 23 **, and 50% of relative humidity, when specific inductive capacity was measured again, it was completely changeless. The elastic moduli by the nano indentation method of this film were 2.5GPa. When the compatibility examination of the siliceous membrane was done using ACT-970 (made by Ashland Chemical) widely used as etching residue release liquid, the etching rate was a part for 0.8A/, and the dielectric constant by the examination concerned was 2.0.

[0047]45 g of comparative example 1 (methyl siloxane polymer / BR1122=4:1) tetramethoxy silanes, 140 g of methyl trimetoxysilane and 18 g of dimethyldimethoxysilane are melted in the isopropyl alcohol 615g, The methyl siloxane polymer solution 40g which trickles the 0.3-N phosphoric acid aqueous solution 60g, made hydrolyze, and was obtained was made to mix the 20% isopropyl alcohol solution 10g of methacrylate (Mitsubishi Rayon BR1122), and it stirred enough. Then, the solution was filtered with the PTFE syringe filter by ADVANTEC Co., Ltd. with a filtering accuracy of 0.2 micrometer. The spin coater was used and applied on the silicon wafer (20.3 cm (8 inches) in diameter, and 1 mm in thickness) (1200 rpm, 20 seconds), and the filtrate was dried at the room temperature (5 minutes). Subsequently, the silicon wafer was heated for 3 minutes on a 280 ** hot plate to 100 ** and the next in atmospheric air (25 **, 40% of relative humidity), respectively. This film was calcinated for 30 minutes at 400 ** among a dry nitrogen atmosphere. The absorption based on Si-O of the wave numbers (cm^{-1}) 1020 and 460 in IR (infrared absorption) spectrum, The absorption based on Si-C of the wave numbers (cm^{-1}) 1280 and 780 and the absorption based on C-H of the wave number (cm^{-1}) 2980 were mainly seen, and the absorption based on BR1122 disappeared. When the obtained film was evaluated, as for 2.3 and density, $2.2 \times 10^8 \text{ dyne/cm}^2$ and the crack marginal thickness of 1.8 g/cm^3 and internal stress were [specific inductive capacity] not less than 1.5 micrometers. After neglecting the obtained film for one week in the atmosphere of the temperature of 23 **, and 50% of relative humidity, when specific inductive capacity was measured again, it was completely changeless. The

elastic moduli by the nano indentation method of this film were 1.8GPa. When the compatibility examination of the siliceous membrane was done using ACT-970 (made by Ashland Chemical) widely used as etching residue release liquid, an etching rate is a part for 3.4A/, and the dielectric constant rose to 2.5 by the examination concerned.

[0048]60 g of perhydropolysilazane compounded by the comparative example 2 (PPSZ-1, LPSZ-1 (0.3) / PMMA=4:1) and the Tori (isopropoxy) aluminum reference example 3 was dissolved in 240 g of xylene, and the polysilazane solution was prepared. Next, mix 3 g of Tori (isopropoxy) aluminum to 147 g of xylene, it was made to dissolve, 6 g was taken out from the inside, and it mixed in the polysilazane solution. Subsequently, the above-mentioned polysilazane solution was mixed and what dissolved well 15 g of poly methyl methacrylate of the molecular weight 100,000 in 60 g of xylene was stirred enough. Then, the solution was filtered with the PTFE syringe filter by ADVANTEC Co., Ltd. with a filtering accuracy of 0.2 micrometer. The spin coater was used and applied on the silicon wafer (10.2 cm (4 inches) in diameter, and 0.5 mm in thickness) (2300 rpm, 20 seconds), and the filtrate was dried at the room temperature (5 minutes). Subsequently, the silicon wafer was heated for 3 minutes on a 220 ** hot plate to 150 ** and the next in atmospheric air (25 **, 40% of relative humidity), respectively. This film was calcinated for 30 minutes at 400 ** among a dry nitrogen atmosphere. The absorption based on Si-O of the wave numbers (cm^{-1}) 1070 and 450 in IR (infrared absorption) spectrum, And the absorption based on Si-H of the wave numbers (cm^{-1}) 2250 and 880 was mainly seen, and the absorption based on N-H of the wave numbers (cm^{-1}) 3350 and 1200 and the absorption based on poly methyl methacrylate disappeared. When the obtained film was evaluated, as for 1.8 and density, $2.7 \times 10^8 \text{ dyne/cm}^2$ and the crack marginal thickness of 1.0 g/cm^3 and internal stress were [specific inductive capacity] not less than 5 micrometers. After neglecting the obtained film for one week in the atmosphere of the temperature of 23 **, and 50% of relative humidity, when specific inductive capacity was measured again, it went up 0.1 times and was 1.9. The elastic moduli by the nano indentation method of this film were 1.9GPa. ACT-970 widely used as etching residue release liquid (made by Ashland Chemical), When the compatibility examination of the siliceous membrane was done using ST-210 and ST-250 (made by ATMI), since all films disappeared also about which medicine, the etching rate was incapable measurement.

[0049]



[Effect of the Invention]The nature film of porous silica obtained by this invention shows very low specific inductive capacity stably, and. Since the mechanical strength which can bear the removal process of the wiring material by the CMP method, and various kinds of chemical resistance are combined, it is useful especially as an interlayer insulation film for semiconductor devices which suits the newest high integration processes including damascene process.

[Translation done.]

